

UNITED STATES PATENT APPLICATION

of

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for

FREE-STANDING DIAMOND STRUCTURES AND METHODS

## CLAIM OF PRIORITY

**[0001]** This application claims the benefit of the filing date priority of U.S. Provisional Application No. 60/445,237 filed February 6, 2003; No. 60/494,089 filed August 12, 2003; and No. 60/494,095 filed August 12, 1003.

## BACKGROUND OF THE INVENTION

**[0002]** The present invention relates to free-standing objects having laboratory grown diamond surfaces and methods for fabricating such objects. More particularly, the present invention is directed to such objects and methods wherein the outer surface of the object includes a plurality of intersecting facets having a diamond layer.

**[0003]** Diamond is one of the most technologically and scientifically valuable materials found in nature due to its combination of high resistance to thermal shock, extreme hardness, excellent infrared transparency, and excellent semiconductor properties.

**[0004]** Diamond has the highest known isotropic thermal conductivity and a relatively low expansion coefficient thus providing it with desirable resistance to thermal shock. Because of these properties, diamond has found increasing use as a thermal management material in electronic packaging of devices such as high power laser diodes, multichip modules, and other microelectronic devices.

**[0005]** Diamond is also the hardest known material and has desirable resistance to abrasion. Thus diamond components and coatings have found increasing use as wear resistance elements in various mechanical devices and in cutting and grinding tools. Diamond is also highly resistant to corrosion.

**[0006]** Diamond is also a good electrical insulator, but can be synthesized to be electrically conducting by the addition of certain elements such as boron to the growth

atmosphere. Diamond is also used in many semiconductor devices including high-power transistors, resistors, capacitors, FET's, and integrated circuits.

**[0007]** The scarcity and high cost of natural diamond has prohibited its widespread commercial use. However, the development of various methods for synthesizing diamond has made the widespread commercial use of diamond possible. The most commercially promising method for synthesizing diamond includes the growth of diamond by chemical vapor deposition (CVD).

**[0008]** Diamond synthesis by CVD has become a well established art. It is known that diamond coatings on various objects may be synthesized, as well as free-standing objects. Typically, the free-standing objects have been fabricated by deposition of diamond on planar substrates or substrates having relatively simple cavities formed therein. For example, U.S. Patent No. 6,132,278 discloses forming solid generally pyramidal or conical diamond microchip emitters by plasma enhanced CVD by growing diamond to fill cavities formed in the silicon substrate. However, there remains a need for methods of making free-standing, internally-supported, three-dimensional objects having an outer surface comprising a plurality of intersecting facets (planar or non-planar), wherein at least a sub-set of the intersecting facets have a diamond layer.

**[0009]** Accordingly, it is an object of the present invention to obviate many of the deficiencies in the prior art and to provide novel methods of making free-standing structures having diamond surfaces.

**[0010]** It is another object of the present invention to provide novel methods of making structures using diamond CVD.

**[0011]** It is yet another object of the present invention to provide novel structures formed by diamond CVD.

**[0012]** It is still another object of the present invention to provide novel methods of making free-standing structures having an exposed diamond surface.

[0013] It is a further object of the present invention to provide novel methods of making internally-supported structures having an exposed diamond surface.

[0014] These and many other objects and advantages of the present invention will be readily apparent to one skilled in the art to which the invention pertains from a perusal of the claims, the appended drawings, and the following detailed description of the preferred embodiments.

#### DETAILED DESCRIPTION OF THE DRAWINGS

[0015] Figure 1 is an illustration showing the steps of the preferred embodiment of the present invention.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] In one aspect, the present invention is directed to methods of making free-standing, internally-supported, three-dimensional objects having a diamond layer on at least a portion of the outer surface of the object. The diamond layer may be formed by any method of synthesizing diamond such as high-pressure, high-temperature (HPHT) methods or CVD. In accordance with the preferred embodiment of the present invention, the diamond is synthesized by CVD.

[0017] In the diamond CVD methods according to the present invention, a mixture of hydrogen and carbon-containing gases is activated to obtain a region of gas-phase non-equilibrium adjacent the substrate on which the diamond will be grown. The carbon-containing gas may be selected from a large variety of gases including methane, aliphatic and aromatic hydrocarbons, alcohols, ketones, amines, esters, carbon monoxide, carbon dioxide, and halogens. Methane is used according to the preferred embodiment of the invention.

[0018] The mixture of gases is energized to obtain a region of gas-phase non-equilibrium adjacent the substrate on which the diamond will be grown. A variety of gas-phase activation techniques may be used and these techniques may be categorized as

either hot-filament CVD, plasma-assisted CVD, or flame CVD. In plasma-assisted CVD the plasma may be generated by a number of energy sources including microwave, radio-frequency, or direct current electric fields.

**[0019]** The substrate may be any material suitable for nucleating and growing diamond such as semiconductor, metal, and insulator materials. Generally, the nucleation rates are much higher on carbide forming substrates (e.g., Si, Mo, and W) than on substrates that do not form carbides. According to the preferred embodiment of the present invention, silicon substrates are used in view of the desirable nucleation rates and well known fabrication techniques of silicon.

**[0020]** The surface of the substrate on which the diamond will be grown may be pretreated by various techniques to enhance diamond nucleation and improve the nucleation density of diamond on the surface. Such methods may include (i) scratching, abrading, or blasting the surface with diamond particles or paste, (ii) seeding the surface with submicron powders such as diamond, silicon, or cBN, (iii) biasing the substrate, (iv) carburization, (v) pulsed laser irradiation, and (vi) ion implantation.

**[0021]** In accordance with the preferred embodiment of the present invention, a free-standing, internally-supported, three-dimensional object is provided having an outer surface comprising a plurality of intersecting facets wherein at least a sub-set of the intersecting facets have a diamond layer of substantially uniform depth. The term “facet” as used herein, includes a surface or face that is either planar or non-planar.

**[0022]** Figure 1 illustrates the various steps of the preferred embodiment of the present invention. With reference to Figure 1, a silicon substrate 10 is fabricated using conventional fabrication techniques to form a mold having an exposed surface 12 defining the sub-set of intersecting facets. A diamond layer 14 of generally uniform thickness is grown over the exposed surface 12 of the substrate 10 by any suitable method such as hot-filament CVD or plasma-assisted CVD.

**[0023]** The exposed surface 12 may be pretreated by any suitable technique to enhance the diamond nucleation and nucleation density on the exposed surface. Typically, the exposed surface is pretreated by seeding the surface with carbon atoms 16. The pretreatment of the exposed surface may be important in order to ensure growth of the diamond in the shape of the sub-set of facets which may be relatively complex.

**[0024]** In some instances, a backing layer 18 may be formed over at least portions of the exposed surface of the newly grown diamond layer to provide structural support to the diamond layer when the substrate is removed. Any material that will adhere to the exposed diamond and enhance the rigidity of the diamond layer 14 is suitable for the backing layer 18 (e.g., epoxy, plastic, viscous polymers that harden, glass, etc.). The backing layer may be electrically conductive or non-conductive as desired.

**[0025]** Once the backing layer 18 is formed as desired, the substrate 10 is removed to expose the surface 20 of the diamond layer 14 grown contiguous to the substrate which has been defined by the mold formed by the substrate. The substrate 10 may be removed by any suitable means such as chemical etching. The diamond layer 14 may then be treated as desired.

**[0026]** The free-standing objects made according to the present invention may find utility in a variety of applications such as backward wave oscillators, bi-polar plates for fuel cells, traveling wave tubes, microchannel plates, and a multitude of other devices having a surface comprising a plurality of intersecting facets wherein a sub-set of intersecting facets have a diamond layer of substantially uniform thickness.

**[0027]** While preferred embodiments of the present invention have been described, it is to be understood that the embodiments described are illustrative only and that the scope of the invention is to be defined solely by the appended claims when accorded a full range of equivalence, many variations and modifications naturally occurring to those of skill in the art from a perusal hereof.